Elastic and inelastic scattering of 4d inner shell electrons in $(Y,Gd)_2O_3$ studied by synchrotron radiation excitation.

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ABSTRACT

Excitations within the 4f shell of Gd^{3+} in $(Y,Gd)_2O_3$ are observed by resonant elastic and inelastic soft x-ray scattering with synchrotron radiation[1]. Inelastic scattering takes place when exciting $4d^{10}4f^7 \rightarrow 4d^9 4f^8$ transitions and extends over an energy range of about 10 eV. The features can be assigned to the net transition from the $^8S_{7/2}$ ground state to the sextet multiplets of the $4f^7$ configuration in Gd^{3+} which have the same parity as the ground state. The inelastic scattering is maximal when the excitation energy is tuned to the $4d^9 4f^8$ (^6D) intermediate state[1].

INTRODUCTION

Rare earth elements are characterized by their partially filled 4f-shell. The 4f electrons are highly localized due to the centrifugal term in the potential and have a low binding energy (about 9 eV in Gd). When a 4d electron is promoted to a 4f state ("4d-4f transition"), the strong interaction of the 4d vacancy with the open 4f shell leads to a complex multiplet structure of 37 terms in triply ionized gadolinium. Due to the strong electron correlation, these 4d-4f transitions produce what is called the "giant resonance", which extends over an energy range of up to 20 eV for some of the rare earth elements. In the case of gadolinium, the 4d ionization threshold is at 151 eV and 156 eV just above the "giant resonance", whose absorption maximum is at 149 eV[2].

In $(Y,Gd)_2O_3$, gadolinium exists as the triply ionized atom (Gd^{3+}) due to the ionic binding to the oxygen atom. The configuration of the outer electrons in Gd^{3+} is $4d^{10}5s^25p^64f^7$, and the half filled 4f shell forms an octet ground state level of $^8S_{7/2}$. The ground state $^8S_{7/2}$ has a spherical symmetry which is very stable and therefore much less affected by the crystal field than ions with an f^6 or f^8 electron configuration. We present the first measurements of ground state excitations to even parity localized final state Gd^{3+} 4f orbitals by high-resolution soft x-ray inelastic scattering. The energy loss mechanisms are explained by our calculations of the energy loss spectra. We have also investigated the variation in the cross sections of these transitions with photon excitation energy. In addition to the inelastic scattering we found that the elastic scattering profile is significantly narrower than the absorption spectrum.

EXPERIMENT

Our experiments were performed at the beamline 8.0 of the Advanced Light Source, ALS, Lawrence Berkeley Laboratory. The undulator beamline is equipped with a spherical grating monochromator[3] with a maximum resolving power of $E/\Delta E = 2000$. The fluorescence end station consists of a Rowland circle grating spectrometer that provides a resolving power of about 400. The incident angle of the p-polarized beam was about 10° to the sample normal.

The absorption spectrum of $(Y,Gd)_2O_3$ in the region where a 4d inner shell electron is promoted to a 4f orbit is shown in Fig. 1 (solid line). The main peak is centered at about 149 eV and has a full

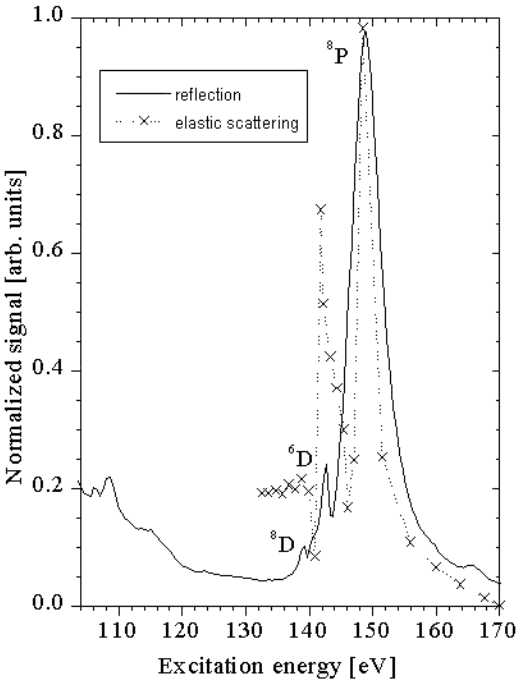

Figure 1: Absorption spectra of $(Y,Gd)_2O_3$ in the photon energy range of the 4d-4f transitions. The terms which characterize the electron configuration of the excited state ($4d^9 4f^8$) are given in the figure. The spectra are obtained by measuring the radiation reflected (solid line) and elastically scattered (X) by the sample.

width at half maximum of about 5.9 eV. The spectrum represents primarily the transition from the ground state $^8S_{7/2}$ to the ^{8}P level. At lower photon energies weaker features occur that result from the excitation of the core electron to the ^{8}D and ^{6}D levels. Transitions from the octet ground state to the sextet state become partially allowed due to the strong spin-orbit interaction.

Fig. 2 shows the soft x-ray energy loss spectra in $(Y,Gd)_2O_3$ in the vicinity of the 4d-4f resonances (134-168 eV). The energy loss (or in other words the excitation energy of the final state) has been obtained by subtracting the energy of the incoming photons (excitation energy) from the energy of the emitted photons. The spectra are normalized to 300 mA of storage ring current and the number of counts is plotted versus the energy loss of the scattered photons. The counting time for each spectrum has been 30 minutes. Three principal types of photon-in photon-out features can be distinguished in all spectra: The peaks of elastically scattered radiation, of inelastically scattered radiation and of fluorescence radiation. The elastically scattered radiation appears at the energy of the exciting radiation, which corresponds to an energy loss of 0 eV. Due to the magnified scale, the elastic peaks are not fully displayed in Fig. 2. Therefore the maximum count rate in the elastic peak at each excitation energy is represented by an X in Fig. 1. The dotted curve in Fig. 1 is drawn through the experimental points to guide the eye. The energetic position of the main features is the same for the elastic scattering curve (dotted line) and the absorption curve (solid line). The $4d^9 4f^8 \rightarrow 4d^{10} 4f^7$ emission is maximal when the excitation energy is tuned to the ^{8}P resonance in the absorption curve where the 4d hole is immediately refilled by the excited 4f electron as it scatters the incoming photon. The peak width for the elastic scattering curve is much smaller (3 eV) than the absorption curve (5.9 eV). The autoionization width found by Richter et al.[3] is 5.2 eV. The different peak width is due to the different final states the excited configuration ($4d^9 4f^8$). It can decay via the main process, autoionization ($4d^9 4f^8 \rightarrow 4d^{10} 4f^6 + e^-$), which produces mostly 4f electrons or via elastic scattering leads to the final state $3d^{10} 4f^7$.

Near threshold the decay of a core hole-state can be very different from the decay mechanisms at higher energies. Soft x-ray emission and (radiationless) Auger-electron emission can appear as coherent one-step processes also known as the (resonant) Raman effect.

The intermediate states correspond to $4d^9 4f^8$ ^{8}D, ^{6}D, and ^{8}P resonance states and the energy loss can be assigned to the difference in energy between the initial and final state often designated as the "net transition". At energies above the threshold, the inelastic scattering evolves into fluorescence, and possible inelastic scattering produced by electron momentum scattering in the Brillouin zone, where soft x-ray inelastic scattering has been used to elucidate band symmetries and probes specific regions of the Brillouin zone.

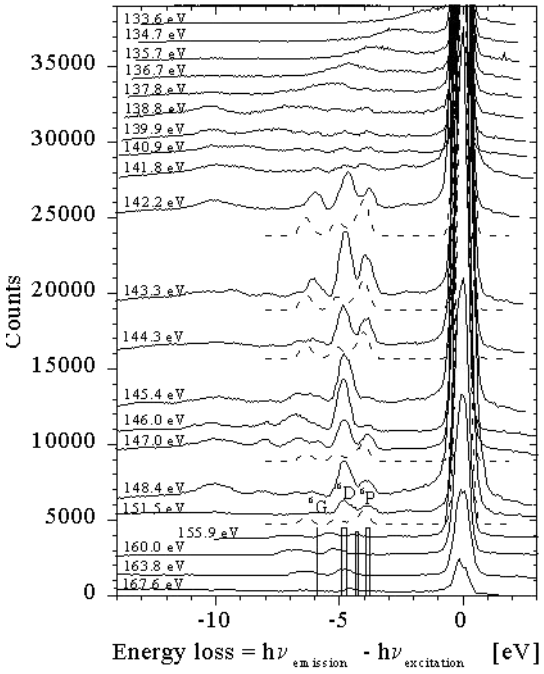

Figure 2: Energy loss spectra on $(Y,Gd)_2O_3$ in the region of the 4d-4f threshold. The excitation energy is given above each spectrum. Calculated energetic positions for the terms that are assigned to the energy losses and represent excitations within the 4f shell are plotted as vertical bars. The dashed lines represent calculated energy loss spectra.

We have calculated the loss spectra[1] using transition probabilities from the ground state to the intermediate states and back to the final metastable states obtained by Cowan's method[4], summing incoherently over all the intermediate states of the $4d^9 4f^8$ configuration.

An onset of three inelastic excitations at an excitation energy of about 139 eV is observed (Fig. 2). These features remain at a constant difference in energy relative to the elastic peak throughout the energy range of excitation. In Gd the 4f shell is half filled and the absence of valence band-electrons in the vicinity of the Gd ion leads to a term scheme with only a few possible excitations. The next terms above the ground state $^8S_{7/2}$ belong to the sextet multiplet: ^6P_J, ^6I_J, ^6D_J and ^6G_J of the same electron configuration $4f^7$. The energetic positions of these states for Gd^{3+}:LaF_3 as calculated by Carnall et al.[6] are plotted in Fig. 2. Optical and UV absorption spectroscopy data and calculations for Gd doped in various compounds show that the energetic differences in this term scheme for the different materials and their different crystal fields are smaller than 0.02 eV which is small compared to our energy resolution (<0.4 eV). The width of the bars in Fig. 2 represents the energy range over which the various J-levels extend for a given term. Reconfigurations within the 4f-shell ("f-f transitions") by photon excitation are dipole forbidden due to the spin selection rule $\Delta S=0$for L-S-coupling. The inelastic scattering produces energy losses of less than 6 eV and is due to net transitions from the $^8S_{7/2}$ ground state (electron configuration: $4d^{10}4f^7$) to the sextet multiplets ^6P_J, ^6D_J and ^6G_J of the $4d^{10}4f^7$ configuration. The transitions occur through the intermediate states ^8D_J, ^6D_J and ^8P_J ($4d^9 4f^8$). Population of the ^6I term of $4d^{10}4f^7$ is not observed because of the large change in orbital momentum this transition would require. Different J-levels of the final states are also not resolved. At excitation energies higher than the peak energy of the 4d-4f excitation (149 eV), the inelastic processes become weaker (151.5 eV), shift in energy loss (above 155.9) and finally disappear (167.6 eV). It is worth noticing that the partial cross sections for the three inelastic excitations behave differently. Only the strongest inelastic peak that comes from the excitation to the ^6D state remains intense over an energy range of about 9 eV. At an excitation energy of about 156 eV the inelastic peaks become very weak and the magnitude of the energy loss changes.

While we observe intense inelastic and elastic scattering as the photon energy is tuned to the 4d-4f resonances ($4d^9 4f^8 \rightarrow 4d^{10}4f^7$), we do not observe fluorescence at excitation energies above the 4d shell ionization threshold due to $4d^9 4f^7 \rightarrow 4d^{10}4f^6$ transitions. This is expected because the partial cross section to produce a 4d hole is small[2] and the 4d hole is filled by competing Auger processes with high probability. A weak fluorescence feature can be seen at an energy loss of 10 eV in the

spectrum taken at 142.2 eV. With smaller excitation energy this peak shifts towards the elastic peak. We suggest that this weak fluorescence feature belongs to a charge transfer state because Gd^{3+} does not offer transitions at this energy. We conclude that in the region of the giant resonance, autoionization and elastic scattering are the dominant interaction mechanisms. Inelastic scattering compared to elastic scattering is weaker by about two orders of magnitude.

To summarize, we have used high-resolution soft x-ray emission spectroscopy with synchrotron radiation to study inner shell 4f excitations of Gd^{3+} in $(Y,Gd)_2O_3$. The soft x-ray emission spectra have been studied when exciting the 4d electrons selectively and strong inelastic features have been observed. According to our calculations, we interpret the energy losses as excitations within the 4f shell. The incident photons excite electrons from the ground state $^8S_{7/2}$ primarily to the intermediate state ^6D_J and are inelastically scattered to the sextet final states $4d^{10}4f^7$ ($^8S_{7/2}$)$\rightarrow 4d^9 4f^8$ (^6D_J)$\rightarrow$ $4d^{10}4f^7$ (^6P_J, ^6D_J, ^6G_J). The energy losses between 4 and 6 eV are due to net transitions from the octet ground state $^8S_{7/2}$ to the low lying sextet terms of the $4f^7$ configuration ^6P_J, ^6D_J and ^6G_J.

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